A Density Functional Study of Small $(NiTi)_x$ Clusters with x= 1—3

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Systematic studies on the geometry, electronic structure and vibrational properties of small $(NiTi)_x$ clusters with x= 1_ 3, within the framework of the density functional theory, were performed in this work. The electronic structure analyses were used to investigate the bonding between the early-late(EL) transition metals in their alloy. The results of our calculations have been used to predict $(NiTi)_x$ clusters structure for the ground state and confirm that *s*-electron density is transferred from Ti atoms to Ni atoms followed by the back donation of electrons through the *d*-orbital. The study provides a fragment approach based on the isolobal analogy that NiTi molecular fragments play a significant role in forming clusters.

Keywords NiTi cluster, DFT, Isolobel analogy
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Introduction

Alloys of early transition metals with late transition metals such as NiTi and ZrTi are useful industrial materials in various fields. NiTi[1] alloys have a superhard character and display a remarkable memory effect, *i.e.*, the alloy may be severely deformed, yet returns to its previous shape when heated. The first reported steps towards the discovery of the shape memory effect were taken in the 1930's, it was only in the mid-1990's that the first widespread commercial applications made their breakthrough in biomedicine. Thus the formation of alloys composed of early-late (EL) transition metals seems to be important due to their interesting material properties.

The bonding model in early-late transition metal bulk was suggested by Brewer and Engel[2], who have found *s*-electron density is transferred from the early transition metal to the late transition metal, followed by back donation of electrons through the *d*-orbital. On the other hand, neither experimental nor theoretical studies[3,4] can provide direct information about the microstructures. It is of benefit to systematically study the electronic, geometrical properties of NiTi clusters. This paper presents a theoretical study of $(NiTi)_x$ cluster, with the density functional theory. The structural, electronic and vibrational properties of the stable isomer are also reported.

Computational Details

Density functional theory(DFT) calculations are performed for small NiTi clusters with the help of the Amsterdam density functional(ADF) package[5], DMOL[6] code and Gaussian 98[7] program. The ADF code is based on Slater-type orbitals (STO) instead of the Gaussian-type functions, the basis set was constructed by triple-ξ STO. The 1*s*, 2*s* and 2*p* atomic orbitals were treated in the frozen core approximation. We used VWN[8] potential as a local part of the exchange and correlation potentials and PW[9] potential was used for gradient correction. For DMOL code, we chose the double numerical basis plus polarization basis set and performed spin-unrestricted calculation including VWN potential and PW91. For Gaussian98, we used the hybrid *ab initio* density-functional B3LYP method, the inner(1*s*, 2*s*, and 2*p*) electrons of Ti, Ni were replaced by an ECP[10]. The 3*s*, 3*p*, 3*d*, 4*s*, and 4*p* shells were treated with a double-zeta, DZ basis. The binding energy(E_B) of a cluster is defined as $E_B = E_t - E_a$, where E_t is the total energy of the cluster and E_a is the sum of energies of individual atoms in the cluster.

Results and Discussion

1 NiTi

A triplet state was found to be the ground state of NiTi, the valence electronic configuration is $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 4\sigma^2 2\pi^4 5\sigma^2 3\pi^4 6\sigma^2 1\delta^4 2\delta^1 7\sigma^1$. Fig. 1

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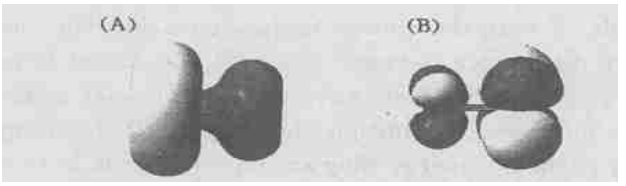

Fig. 1 HOMO(A) and SOMO(B) of NiTi.

shows the highest energy occupied molecular orbital(HOMO) 7σ and the second occupied molecular orbital(SOMO) 2δ. The HOMO is a σ *s*-*d* hybrid orbital and SOMO is expected to be a weakly antibonding $d\delta$-$d\delta$ orbital. In the case of triplet state, the spin density is located on the titanium atom, 0.304 e charges transfer occurs from Ti to Ni. The natural electronic configuration of Ti is $4s^{1.12}3d^{2.55}4p^{0.02}$, while that of Ni is $4s^{1.19}3d^{9.11}$.

It can be seen from Table 1 that a variety of DFT calculation results can be used to predict that the Ni_ Ti bond lengths are very similar, about 203 pm, the vibrational frequency results from the calculations are quite consistent with the experimental values[11]. The binding energies of the ground state have a marked difference, and the calculations reveal DMOL results less than other corresponding results attributed to electron smearing technique. GGA values show better results of binding energies, an improvement over LDA.

Table 1 Comparison of bond length, binding energy, vibrational frequency of NiTi ground state with different theoretical calculations

Method	Spin multiplicity	Symmetry	R/pm	E_B/eV	ω_e/cm^{-1}
ADF-VWN	3	$^3\Delta_g$	201	4.43	366
ADF-PW91	3	$^3\Delta_g$	207	3.98	343
DMOL-VWN	3	$C_{\infty v}$	202	3.11	386
DMOL-PW91	3	$C_{\infty v}$	207	2.09	355
G98-VWN	3	$^3\Delta_g$	201	4.84	382
G98-PW91	3	$^3\Delta_g$	207	3.46	349

2 Ni_2Ti_2

The equilibrium geometries for Ni_2Ti_2 isomers are given in Fig. 2. The bond lengths are given in nanometer. Table 2 summarizes the energies and vibrational frequencies for Ti_2Ni_2 isomers . Structure D is the most favored geometry, the Ti_ Ti bond length(217 pm) is between the bond length of bent structure F(251 pm) and the bond length of linear structure G(195 pm). The vibrational analysis performed on this structure yielded real frequencies, indicating that it is a true minimum. The valence electronic configuration is $8A_g^2 1A_u^2 2B_{1g}^2 6B_{1u}^2 2B_{2g}^2 4B_{2u}^2 3B_{3g}^2 4B_{3u}^2$.

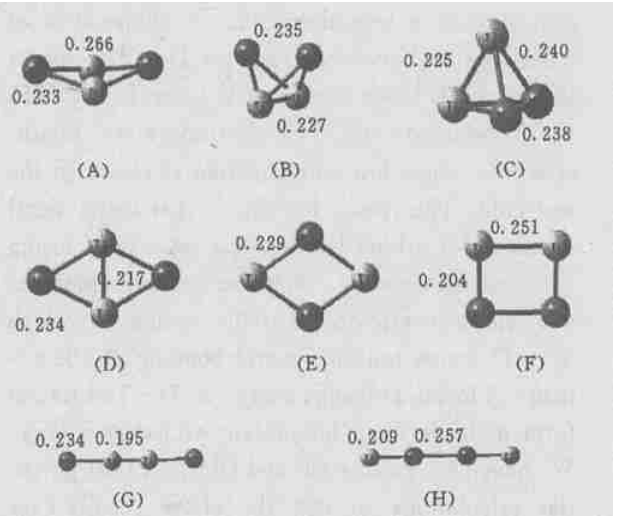

Fig. 2 Optimized geometries for the isomers of Ni_2Ti_2 cluster at Gaussian 98 PW91 level.

Table 2 Absolute energies(Hartree), frequencies(cm^{-1}) and zero point energy(ZPE)(kJ/mol) for various isomers of Ti_2Ni_2 cluster

Structure	Symmetry+electronic state	Absolute energy(ZPE)	Frequencies
A	C_{2v} $^3A_1$	−454.922(7.312)	59, 85, 153, 222, 322, 382
B	C_{2v} $^1A_1$	−454.904(7.900)	24, 117, 152, 256, 265, 382
	C_{2v} $^3B_1$	−454.918(7.399)	39, 121, 157, 213, 330, 378
	C_{2v} $^5A_2$	−454.892(6.772)	136i, 162, 167, 207, 241, 353
C	C_1 3	−454.911(7.231)	93, 146, 155, 170, 274, 370
	C_1 5	−454.914(7.691)	82, 157, 171, 222, 274, 378
D	D_{2h} ^1A_g	−454.924(7.775)	18, 148, 164, 221, 336, 414
	D_{2h} $^3B_{2g}$	−454.912(6.981)	34, 112, 154, 185, 330, 352
	D_{2h} $^5B_{3g}$	−454.920(6.772)	38, 106, 148, 176, 331, 335
E	D_{2h} $^3B_{2u}$	−454.776(5.643)	187i, 131, 138, 190, 220, 264
	D_{2h} $^5B_{3g}$	−454.921(6.772)	38, 106, 148, 176, 331, 335
F	C_s $^1A'$	−454.886(7.399)	24i, 132, 182, 236, 335, 356
	C_s $^3A''$	−454.878(6.604)	62, 113, 119, 187, 284, 343
G	$D_{\infty h}$ $^1\Sigma_g$	−454.770(6.668)	5i, 5i, 82, 82, 152, 234, 572
	$D_{\infty h}$ $^3\Sigma_g$	−454.823(5.141)	22i, 18i, 61, 71, 107, 185
H	$D_{\infty h}$ 5	−454.652(4.473)	175i, 14, 26, 100, 153, 197

A natural population analysis has been done to obtain the charges on Ti(0.38 e) and Ni(− 0.38 e) of ground state in structure D, and the natural electronic configuration of Ti is $4s^{0.63}3d^{2.93}4p^{0.03}$, while that of Ni is $4s^{1.22}3d^{9.15}$. Fig. 3 exhibits HOMO and SOMO of Ni_2Ti_2. It is clear that the bond of Ti_ Ti is formed from the σ and δ orbitals of the NiTi fragment. The other comparative isomer is structure E the bond energy of which is 0.1 eV above that of structure D, the vibrational analysis also showed a true minimum. A comparison of bond lengths between structures D and E shows that model E has a significantly large Ti_ Ti(255 pm) bond length and a $^5B_{3g}$ electronic state, in other words, there are four unpaired electrons in the molecule. The reason for this is that metal-metal forms a d-d orbital bond at the expense of losing d-d exchange energy. So there exists a comparative relative energy in the stable isomers, in which Ti_ Ti forms multiple metal bonding at the expense of losing exchange energy or Ti_ Ti does not form multiple bond but obtain exchange energy. We have performed ADF and DMOL PW91 potential calculations to test the above results (see Fig. 4). Optimization leads to a stable minimum on model E with the quintet multiplicity, and the energy difference between model E and model D is very small about 0.04 eV. It is obvious that forming metal-metal multiple bonding and obtaining d-d exchange energy play an important role in this type of alloy cluster formation.

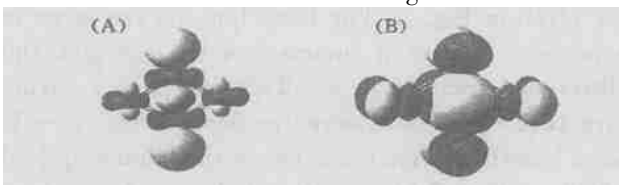

Fig. 3 HOMO(A) and SOMO(B) of Ni_2Ti_2.

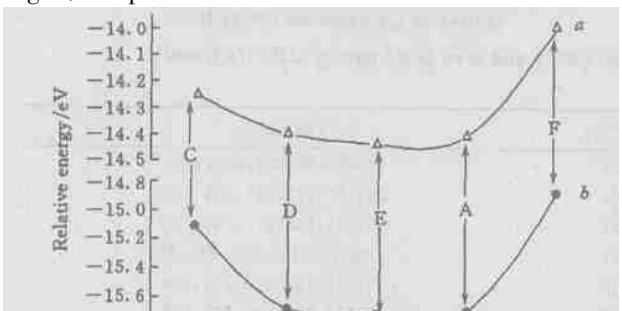

Fig. 4 Plot of the relative energies(eV) of the various isomers of Ni_2Ti_2 cluster by means of ADF PW91 (*a*) and DMOL PW91(*b*).

3 Ni_3Ti_3

Several stable isomers were found for the Ni_3Ti_3 cluster. Fig. 5 shows the equilibrium geometries for these isomers. The bond lengths are given in nm. The absolute energies of the ground states and some low-lying states in different symmetries are shown in Table 3. The lowest energy isomer of Ni_3Ti_3 corresponds to the non symmetric one, C_1 structure(B) that distorts along the C_{2v} structure turns out to be a true minimum in energy after the vibrational analysis.

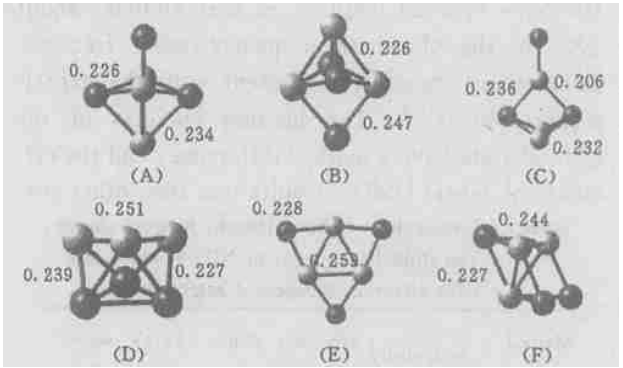

Fig. 5 Optimized geometries for the structures of the isomers of Ni_3Ti_3 cluster.

A similar result as above is achieved during the computation, that is, HOMO and SOMO of Ni_3Ti_3 are composed of σ and δ orbitals(see Fig. 6). A natural population analysis has been done to obtain the charges on Ti(0.45 e, 0.09 e) and Ni(− 0.43 e, − 0.12 e), and the natural electronic configuration of Ti is $4s^{0.8}3d^{2.90}$, $4s^{1.1}3d^{2.86}$, while that of Ni is $4s^{0.95}3d^{9.13}$, $4s^{1.08}3d^{9.10}$.

Fig. 6 HOMO(A) and SOMO(B) of Ni_3Ti_3.

Table 3 Absolute energies(Hartree), image vibrational frequencies(cm^{-1}) and total spin in different symmentries

Symmetry	C_{2v}(A)		C_1(B)		C_{2v}(C)	C_s(D)	D_{3h}(E)	C_s(F)	
S	0	1	0	1	0	0	1	1	2
Energy/H	− 682.48	− 682.46	− 682.50	− 682.51	− 682.39	− 682.48	− 682.44	− 682.48	− 682.47
Image frequencies/cm^{-1}		83i	53i		86i, 32i			67i	39i

It can be seen that the structures of $(NiTi)_x$ (x= 1- 3) clusters can be built with NiTi molecular fragment which is an isolobal analogy to alkenes(shown in Fig. 7). So we can build a large

size NiTi cluster making use of THE analogy method.

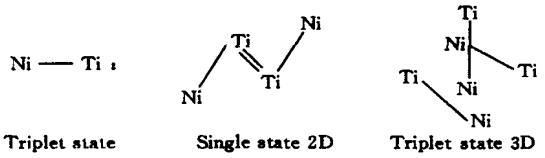

Fig. 7 Schematic structures of NiTi molecular fragment.

The charge transfer process of the Brewer-Engel model can be confirmed in our work, *s* electron density is transferred from Ti to Ni atom. Moreover atom Ti has the empty *d* orbital to obtain electrons by back donation. As mentioned above, the titanium atom allows $d\sigma$-$s\sigma$ hybridization, leading to a partial transfer of s electrons to the nickel atom. As the cluster size increases, Ti atom *s*-orbital character is reduced through *s*-*d* hybridization by reason of increasing coordination numbers, thus increasing the charge transfer to the Ni atom. At the same time, Ni *d* orbital overlaps with Ti $d\delta$ orbital to realize back donation.

Conclusions

We examined the geometric and electronic structures of $(NiTi)_x$ clusters(x= 1_ 3) by using density-functional calculations and three different theoretical methods. DFT reasonably predicts the structure and electronic properties of cluster NiTi, and the use of the PW91 functional would prove its value in the study of these types of alloy systems. The calculated results confirm *s*-electron density is transferred from the Ti atom to the Ni atom followed by back donation of electrons through the *d*-orbitals. This study provides a fragment approach to construct the equilibrium structures, namely, NiTi dimer can act as a molecular fragment, which is an isolobal analogy to $C{=}CH_2$ and can be polymerized. Therefore, it is concluded that the NiTi molecular fragment plays a significant role in forming clusters. Future work involving large NiTi clusters has been being performed to investigate more evidence in this approach, it helps to analyze the growth species and the clustering phenomenon.

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